MODELING PRESSURE-IONIZATION OF HYDROGEN IN THE CONTEXT OF ASTROPHYSICS

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The recent development of techniques for laser-driven shock compression of hydrogen has opened the door to the experimental determination of its behavior under conditions characteristic of stellar and planetary interiors. The new data probe the equation of state (EOS) of dense hydrogen in the complex regime of pressure ionization. The structure and evolution of dense astrophysical bodies depend on whether the pressure ionization of hydrogen occurs continuously or through a "plasma phase transition" (PPT) between a molecular state and a plasma state. For the first time, the new experiments constrain predictions for the PPT. We show here that the EOS model developed by Saumon & Chabrier can successfully account for the data, and we propose an experiment that should provide a definitive test of the predicted PPT of hydrogen. The usefulness of the chemical picture for computing astrophysical EOS and in modeling pressure ionization is discussed.

Keywords: Equation of state; hydrogen; effective potentials; pressure ionization; plasma phase transition

1. INTRODUCTION

A series of shock-compression experiments conducted at the Lawrence Livermore National Laboratory has revived much interest in the equation of state (EOS) of hydrogen in the regime of pressure ionization. Over the last three years, measurement of the shock temperature [1], the shock reflectivity [2] and conductivity [3] have been made, and pressures above 1 Mbar have been achieved repeatedly [4,5]. These experiments directly probe conditions of pressure and temperature of great astrophysical interest.

Astrophysical objects in which pressure dissociation/ionization of H takes place range from very-low mass stars ($M \lesssim 0.3\,M_\odot$, where $M_\odot$ is the mass of the Sun) to brown dwarfs (which have masses below $\sim 0.07\,M_\odot$), and extrasolar giant planets down to Jupiter ($0.001\,M_\odot$) and Saturn ($0.0003\,M_\odot$). All of these objects share the same gross composition of $\sim 90\%$ H and $\sim 10\%$ He by atomic fraction. The thermodynamics of hydrogen in the regime of pressure ionization bears on the mechanical and thermal properties of these bodies and determines their interior structure and their evolution. It also directly affects our knowledge of the inner composition of Jupiter and Saturn [6] and theories of their formation processes.

The main aspects of the problem of pressure ionization and its astrophysical significance can be grasped by considering the phase diagram of fluid hydrogen (Figure 1). At relatively low pressures ($P \lesssim 0.1\,\mathrm{Mbar}$), the fluid is fairly ideal. As the temperature is raised, molecules dissociate into atoms which then ionize to form a weakly-coupled plasma. At pressures above $\sim 1\,\mathrm{Mbar}$, non-ideal effects dominate and hydrogen is pressure ionized into a dense plasma. The physical conditions in the plasma are given by the plasma coupling parameter Γ and the electron degeneracy parameter θ. Figure 1 shows that the pressure-ionized plasma is partially to strongly degenerate ($\theta \lesssim 1$) and strongly coupled ($\Gamma > 1$). In the region near $P \sim 1\,\mathrm{Mbar}$ and $\log T \lesssim 5$ the fluid is composed of a mixture of molecules,

atoms, protons and electrons, all strongly interacting. This EOS regime is crossed by the interior profiles of Jupiter, brown dwarfs and very-low-mass stars (dotted lines). The relevance of the new shock-compression data is shown by the calculated principal and reflected Hugoniots [7] corresponding to the experiments (up to 3.5 Mbar)[1,4,5,8].

2. AN EOS BASED ON THE CHEMICAL PICTURE

The work presented here is based on a single, self-consistent free energy model developed a decade ago which describes a strongly-correlated mixture of H_2, H, H^+ and electrons [9,10,11]. This model is based on the so-called "chemical picture," which assumes that the species considered remain chemically distinct under all conditions. In practice, this means that the contributions of the bound states and of the interparticle interactions to the grand partition function of the system can be factorized [12]. In reality, interactions and the spectrum of bound states are coupled and are not strictly factorizable. When the coupling is weak, various corrections to the exact factorizability can be applied very successfully. In the regime of pressure ionization, which, by definition, is characterized by very strong coupling between interactions and bound states, the chemical picture breaks down.

On the other hand, equation of state models based on first-principle approaches consider only electrons and nuclei and solve the Schrödinger equation for bound and free electronic states of a N-body Coulomb system within some approximations. Examples of such "physical picture" models are the activity expansion [13] and quantum Monte Carlo simulations [14]. With increased sophistication, the physical picture is expected to ultimately provide an "exact" description of the phenomenon of pressure ionization. In low-mass stars, brown dwarfs and giant planets, the range of physical conditions encountered compellingly points to an EOS based on the chemical picture, however. These bodies span a wide range of EOS regimes (see Figure 1) which no single model based on

the physical picture can presently accommodate. Since the chemical picture is known to work extremely well at relatively low densities [15,16], for the pure molecular fluid [17], and that it reduces to the physical picture for the fully ionized plasma, it is still the most attractive approach for generating an EOS for many astrophysical applications. For this reason, nearly all EOS's developed over the past 30 years for applications to stellar interiors have been based on the chemical picture.

Since its conception about forty years ago [18], EOS's based on the chemical picture have become rather sophisticated in their treatment of the coupling between interactions and bound states, resulting in very accurate EOS's at relatively low densities [19]. Difficulties arise when these models are pushed into the strongly coupled regimes where approximations valid at low density become inaccurate, diverge or lead to unphysical results. An example is the description of interactions between particles with bound states using pair potentials at low densities while it is known that many-body effects become important at high densities. Within the chemical picture, many-body effects can be accounted for by using *effective* pair potentials obtained by fitting experimental data with a particular EOS model. In this procedure, any physics missing from the EOS model becomes absorbed in the effective potential. It follows that a carefully-constructed chemical picture EOS model, fitted to all the relevant experimental data (which currently cover a very limited part of the phase diagram), will provide a reasonably accurate EOS for astrophysical purposes. Such a model represents a sophisticated and physically-based form of "interpolation" across the regime of pressure-ionization. The reliability of the EOS in this regime depends entirely on the availability of experimental data in appropriate regimes of pressure and temperature. In this context, the recent work on shock-compression of deuterium fills a great void.

2.1. The Free Energy Model

The free energy model developed by Saumon and Chabrier (SC) and the resulting hydro-

gen EOS have been described thoroughly elsewhere [10,11,12] and only a brief outline will be given here. Within the (P,T) region shown in Figure 1, the EOS is derived from a single expression for the Helmholtz free energy of a mixture of H_2, H, H^+ and electrons. The main features of the model include 1) Finite-temperature Fermi-Dirac statistics for the electrons; 2) Realistic interaction potentials for the neutral particles (H_2 and H), with the correlation free energy described with a two-component fluid perturbation theory; 3) A detailed treatment of the internal partition function of H and H_2; including 4) An occupation probability formalism to describe the effects of interparticle interactions on bound states [20]; 5) The Two-Component Plasma model (TCP) describes the low-density, fully ionized plasma; 6) The high density plasma is described with a Screened One Component Plasma model (SOCP); in which 7) The electron screening is described by the linear perturbation theory using a finite-temperature dielectric function and a local field correction; 8) Exchange and correlation terms for the quantum electron fluid; and 9) A polarization potential for the interaction between charged and neutral particles. The chemical equilibrium of the system at a given density and temperature is obtained by minimizing the fully non-ideal Helmholtz free energy. All equilibrium thermodynamic quantities can then be obtained by differentiation of the free energy using well-known expressions.

Central to the calculation of the thermodynamics of the dense, partially dissociated/ionized fluid are the three potentials $\phi_{ij}(r)$ between the neutral particles ($\{i,j\} \equiv \{\mathrm{H}, \mathrm{H}_2\}$). They can be obtained from *ab initio* quantum mechanical calculations for a pair of particles (*e.g.* two molecules). Such potentials, which do not include the many-body effects, are known to be too repulsive at short range [17]. At the time the SC model was developed, the only available effective potential was $\phi_{\mathrm{H}_2-\mathrm{H}_2}$, derived by fitting a thermodynamic model to shock-compression data [17]. *Ab initio* potentials were used for $\phi_{\mathrm{H}_2-\mathrm{H}}$ and $\phi_{\mathrm{H}-\mathrm{H}}$ [21,22].

2.2. Pressure Ionization

The most remarkable prediction of this EOS model is that pressure ionization of H occurs through a first-order phase transition between an insulating molecular phase and a partially-ionized, mostly dissociated, conducting phase [9,10,11]. This so-called plasma phase transition (PPT) is a robust prediction of the model. No reasonable variation of the model, such as changes in the neutral-charged interactions and in the interaction potentials between H and H_2, has produced an EOS without a PPT [11], A qualitatively similar transition is also found in Quantum Monte Carlo simulations of hydrogen [14].

Whether pressure ionization of H occurs continuously or through a PPT remains one of the major unanswered questions in our understanding of the properties of matter under extreme conditions. The answer has profound astrophysical implications. The PPT, if it exists, takes place in the interiors of brown dwarfs and giant planets (Figure 1) and would have important consequences on their structure and evolution [23,24,25]. Unfortunately, no present experimental evidence directly addresses this question. Conductivity measurements of shock-compressed H_2 and D_2 up to 1.8 Mbar show a *continuous* transition in the measured electrical conductivity from a semi-conducting to a conducting state [3]. This result, however, does not preclude the existence of a *structural* transition like the PPT. The increase in conductivity occurs in a very weakly dissociated phase (dissociation fraction $\sim 5\%$), revealing a conducting *molecular* phase. This is consistent with electronic conduction caused by electrons delocalized from H_2^+ ions, a feature reminiscent of the decreasing band gap with increasing pressure in solid H_2 [26]. The conductivity remains constant above 1.4 Mbar up to the largest pressure reached (1.8 Mbar) but is significantly smaller than that expected from a *fully dissociated* H plasma. This strongly suggests that the monoatomic metallic state lies at pressures higher still, a possibility entirely consistent with our PPT calculation.

A "linear-mixing" model has been formulated by Ross [1,27,28] to explain the general features revealed by recent shock-compression experiments which are discussed below. This model interpolates between a purely molecular model and a fully ionized monoatomic model, which are the proper limits of the data at low and high densities, respectively. This interpolation is done by a linear mixing of the molecular and metallic free energies, including an ideal entropy of mixing term and adjusting an entropy parameter to fit the shock-compression data [1]. While the molecular and metallic limits of this model share similarities with the SC free energy, it predicts a continuous transition between the molecular state and the plasma state. This is because the linear-mixing model excludes any critical behavior *by construction*.

3. COMPARISON WITH SHOCK-COMPRESSION EXPERIMENTS

3.1 The Original EOS Model

Figures 2 and 3 show the PPT (dotted line) and compare the calculated principal Hugoniot of deuterium (dashed line) [9,10,11,12] with the experimental (P, ρ, T) data [1,4,5,29]. The calculated Hugoniot is just subcritical and shows significant density and temperature jumps across the PPT. While the agreement of the theory with the (P, T) data is very good, a systematic shift to lower densities is seen for $P > 1.5\,\mathrm{Mbar}$ in Figure 2. Ionization increases along the Hugoniot above 1 Mbar and the Hugoniot asymptotically reaches the limiting compression ratio between final and initial states of $\rho/\rho_0 = 4$ ($0.68\,\mathrm{g/cm^3}$ here), the value for a fully-ionized, high temperature plasma. The maximum compression ratio of the experimental Hugoniot (~ 5.8) agrees remarkably well with the prediction of the model. This generally good agreement validates the treatment of non-ideal effects and pressure dissociation/ionization in the SC EOS. Even considering the experimental uncertainties, however, the (P, ρ) data show no evidence of an upturn in the Hugoniot at $\rho \approx 0.7\,\mathrm{g/cm^3}$ or for the discontinuity across the PPT (Figure 2). This indicates that the critical point

must be below the calculated value of $T_c = 15300\,\mathrm{K}$, and $P_c = 0.615\,\mathrm{Mbar}$ [11]. These experimental results are the very first to provide a constraint on any calculation of the PPT.

3.2 Effective Pair Potentials Fitted to Temperature Data

The first measurements of the temperature of shock-compressed deuterium are compared to the single- and double-shock Hugoniots computed from the original SC EOS [12] in Figure 4 (the same Hugoniots are also shown in Figure 1). The reflected-shock temperatures [1] are about 30% below the values predicted by the original model EOS (dotted curve). The same Hugoniots are also shown in Figure 1. These measurements clearly indicate that the kinetic energy of the shock is partly absorbed in the dissociation of molecules rather than being transferred to their thermal motion. In this experiment [1], the dissociation fraction reaches 20–25%; large enough to allow a determination of *effective* H_2–H and H–H potentials. Thus, considerably softer effective pair potentials $\phi_{H_2-H}(r)$ and $\phi_{H-H}(r)$ were obtained by fitting the temperature data shown in Figure 4. The resulting Hugoniots are shown by solid lines in Figure 4. The figure shows three double-shock Hugoniots and their corresponding initial states along the single-shock Hugoniot (three of the data points repeat the same measurement). The new effective potentials give a very good agreement with the data, except for the double-shock point represented by a triangle, which may be anomalous (a similarly poor fit of this point is found in the original analysis of this data [1]).

The PPT coexistence curve and principal Hugoniot calculated with the same Helmholtz free energy model but using the new effective potentials are shown as solid lines in Figures 2 and 3. The PPT is mildly affected and the critical point is now at $T_c = 14600\,\mathrm{K}$ and $P_c = 0.730\,\mathrm{Mbar}$. The new Hugoniot is barely supercritical and is therefore continuous. In the (P, T) plane, the Hugoniot remains in excellent agreement with the data and the

agreement with the (P, ρ) data is much improved. We emphasize that the Hugoniot shown by the solid curves in Figures 2 and 3 is not fitted to the data shown in these figures, but obtained by fitting the $\phi_{H_2-H}(r)$ and $\phi_{H-H}(r)$ to an independent data set [1] measured in a different (P, T, ρ) regime (see Figures 1 and 4). The linear-mixing model of Ross [27], which is also adjusted to fit the temperature measurements shown in Figure 4, reproduces the experimental single-shock Hugoniot of Figures 2 and 3 just as well as our model [5,29].

For the first time, experimental data which probe the (P, T) domain characteristic of the PPT are available. They clearly show that the earlier determination of the critical point [9,10,11], based on potentials determined from experiments done 16 years ago [8,17] overestimated T_c. Figure 2 suggests that the revised critical point may still be somewhat too hot. The ability to make such statements represents a major step forward in our understanding of the pressure ionization of hydrogen.

The new techniques developed to reach pressures of several Mbar in shock compression experiments [4] open the possibility of a direct detection of the PPT by generating a reflected shock [30]. A shock reflected from the principal Hugoniot at $P \sim 0.36\,\mathrm{Mbar}$ and reaching pressures of up to 3 Mbar would provide a conclusive test of the existence of the PPT as predicted by this model. The reflected Hugoniot reaches the PPT at $T = 9000\,\mathrm{K}$, well below the calculated critical point. The density and temperature discontinuities in the reflected Hugoniot at the transition are $0.6\,\mathrm{g/cm^3}$ and 1700 K, respectively, which should be larger than the experimental uncertainties.

4. FUTURE DEVELOPMENTS

The most significant improvement envisioned for the model is the introduction of the dissolution of the upper bound states of the hydrogen atom by interactions with the surrounding plasma. This can be done following a formalism describing the Stark ionization of these states by the fluctuating microfield [12,20]. This physical mechanism is important

in the regime of temperature ionization even at low densities and will bring the SC EOS in excellent agreement with the very accurate activity expansion EOS [13].

The most natural way to improve the accuracy of this EOS in the regime of pressure ionization is to further modify the H–H interaction potential. Similarly, the coupling between charged and neutral particles (a polarization potential here) could be modified, although several alternatives have already been explored [11]. This should allow a better fit of the data shown in Figures 2 and 3. For the reasons outlined in §2, there is little to gain by increasing the level of sophistication of the model in an attempt to better model pressure ionization within the chemical picture.

The recent experiments [5,29] have revealed that the current theories for dense fluid hydrogen strongly disagree with each other in the regime of pressure dissociation/ionization. With the exception of this work and of the linear-mixing model [27], they agree poorly with the data. The guidance of experimental data is therefore essential to the development of a good understanding of this phenomenon. This need is most acute for models based on the chemical picture, which depend on experiments for the determination of effective pair potentials. The chemical picture is well-suited for the computation of large EOS tables for astrophysical applications, but models must be calibrated with experimental data if they are to be reliable in the difficult regime of pressure ionization. From this perspective, the recent shock-compression data are extremely valuable and it is hoped that this part of the phase diagram will soon be better charted by new experiments.

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Figure Captions

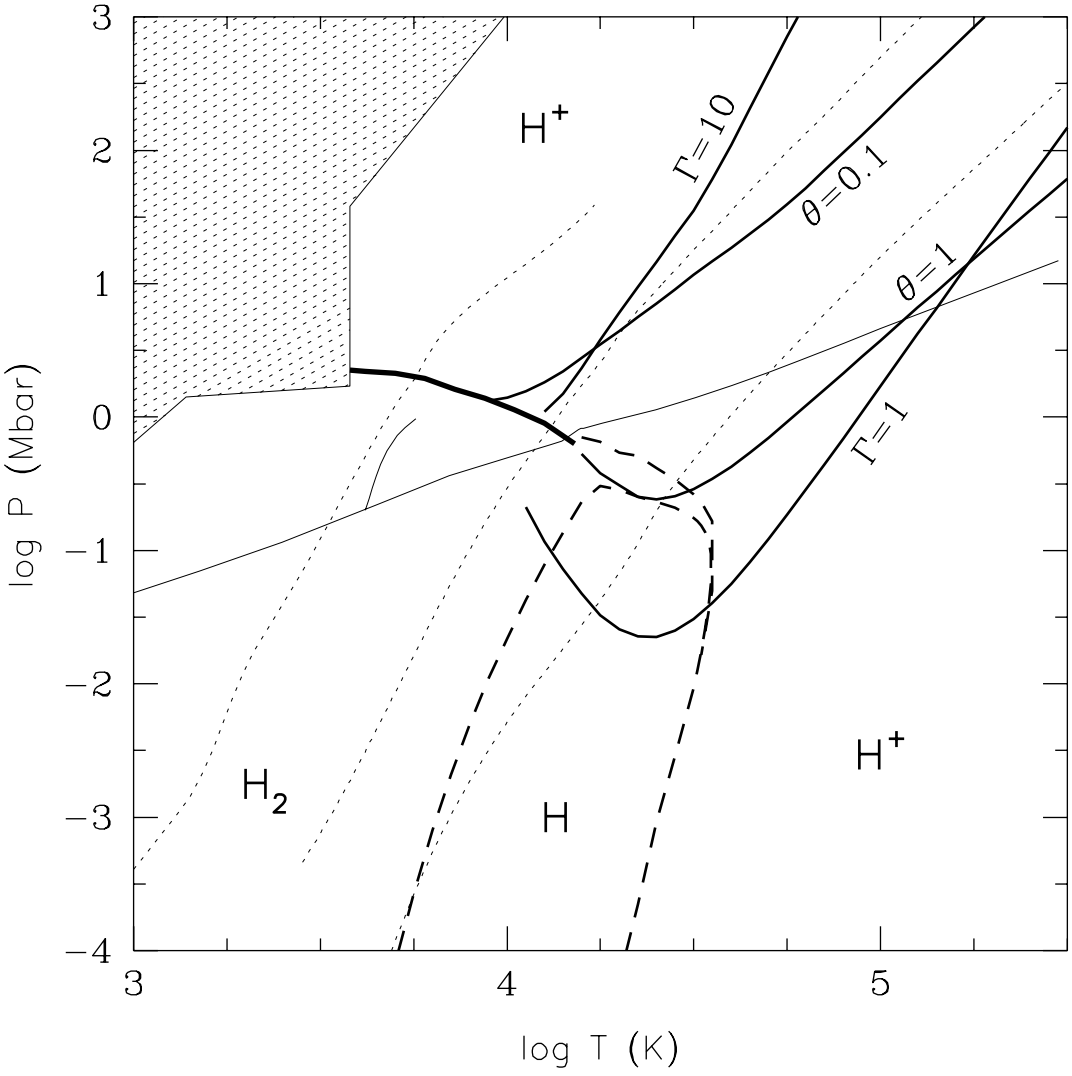
Figure 1: Phase diagram of hydrogen. The coexistence curve of the plasma phase transition (PPT) appears at the left of center as a heavy solid line which ends at the critical point. Curves of constant plasma coupling parameter (Γ) and electron degeneracy parameter (θ) are shown. The plasma coupling parameter is a measure of the strength of the Coulomb interaction. It is defined by $\Gamma = e^2/akT$, the ratio of the electrostatic energy of two protons at the average interionic distance a to their kinetic energy. The electron degeneracy parameter is the ratio of the temperature to the Fermi temperature, $\theta = T/T_F$. Regions dominated by molecules, atoms and ionized H are labeled and delimited by a dashed curve which corresponds to 50% dissociation or ionization. The calculated single- and double-shock Hugoniots corresponding to the experiments are show by the thin solid curves. Finally, the thin black dotted lines show the internal structure profiles of several astrophysical bodies (from left to right): Jupiter, a 7×10^9 yr old brown dwarf of $0.055\,M_\odot$, and a $0.1\,M_\odot$ star. The EOS model is invalid in the hashed region.

Figure 2 : Pressure-density diagram for deuterium showing the single-shock data [5], calculated Hugoniots and the PPT. The Hugoniot based on the EOS of Ref. [12] and the corresponding metastable region of the PPT are shown by dashed and dotted curves, respectively. This Hugoniot is subcritical. After fitting potentials to the measurements of [1] the new EOS model predicts that the Hugoniot is supercritical, as shown by the solid curve. The hashed area shows the new metastable region which has a higher critical density. Note that this is a projection of a (P, T, ρ) surface. With increasing pressure, the Hugoniots come out of the page while the PPT goes into the page.

Figure 3 : Same as Fig. 2 but in the temperature-pressure plane. The coexistence curves of Ref. [12] and the new calculation presented here are shown by the heavy dotted and solid lines, respectively. The bend in the supercritical Hugoniot is caused by the

negative sign of $dP/dT|_\rho$ in the vicinity of the critical point. This behavior is found in some materials and is not thermodynamically forbidden.

Figure 4: Fit to the temperature measurements along the single- and double-shock Hugoniots of D_2 [1]. Each double-shock point corresponds to one of the first-shock points shown. Matching pairs of single and double-shock points are shown with a common symbol. The specific volume V is not measured in the experiment and the error bars in V are taken from (P, V) measurements in a similar experiment [8] and are approximate. Calculated double shocks reflected from $V = 7.98$, 7.44 and $7.10\,\mathrm{cm}^3$/mole along the principal Hugoniot are shown.


H+
Γ=10
θ=0.1
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log P (Mbar)
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2
1
0
−1
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−3
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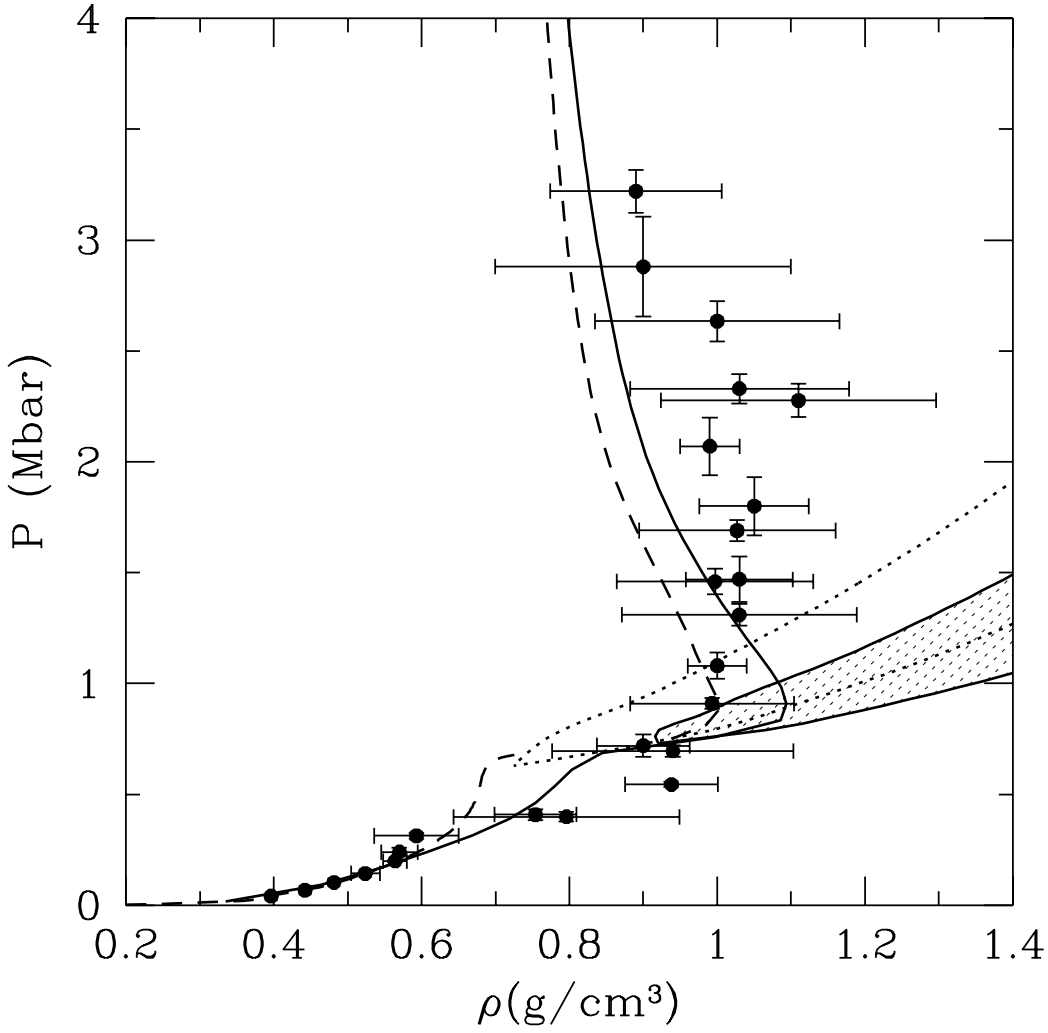
5


4
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P (Mbar)
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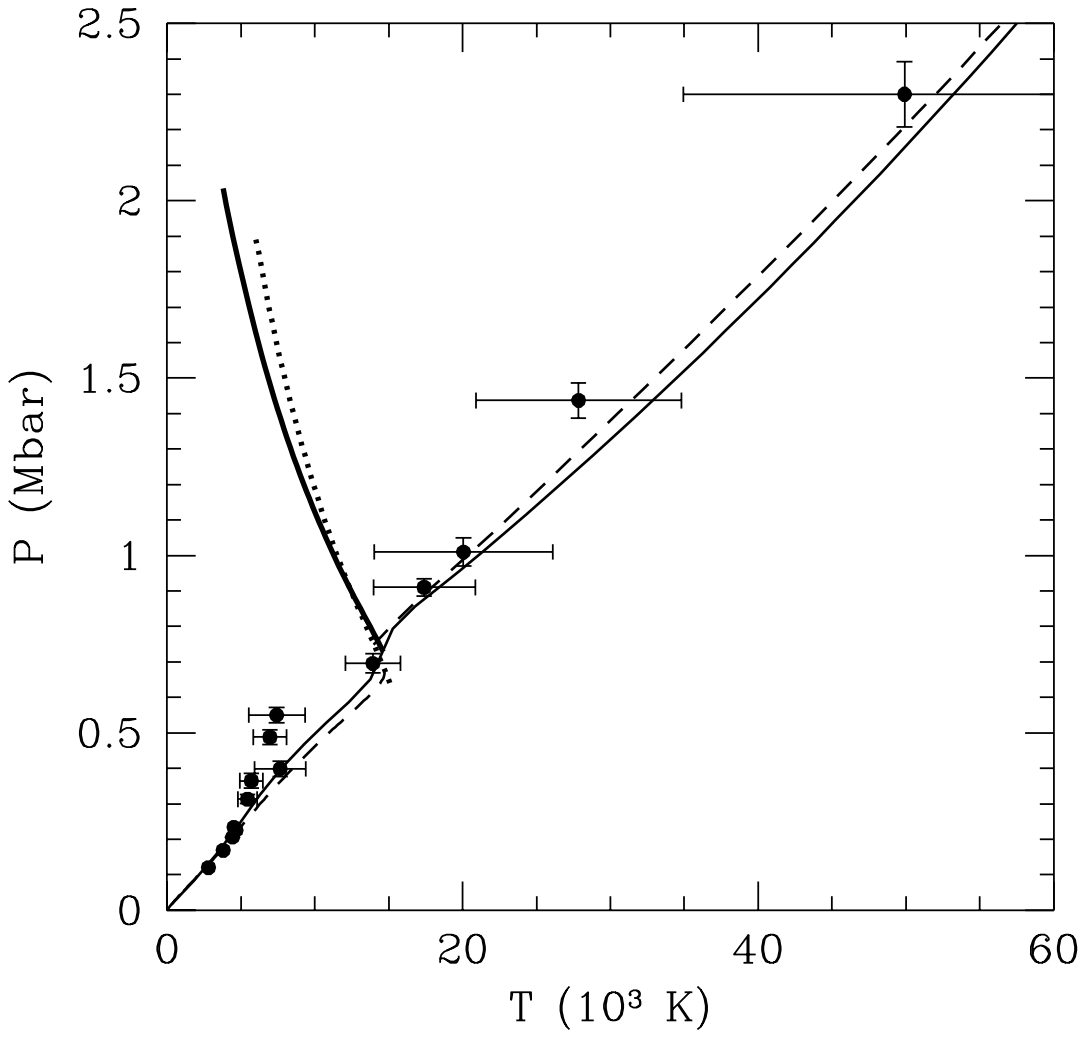
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1.5
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P (Mbar)
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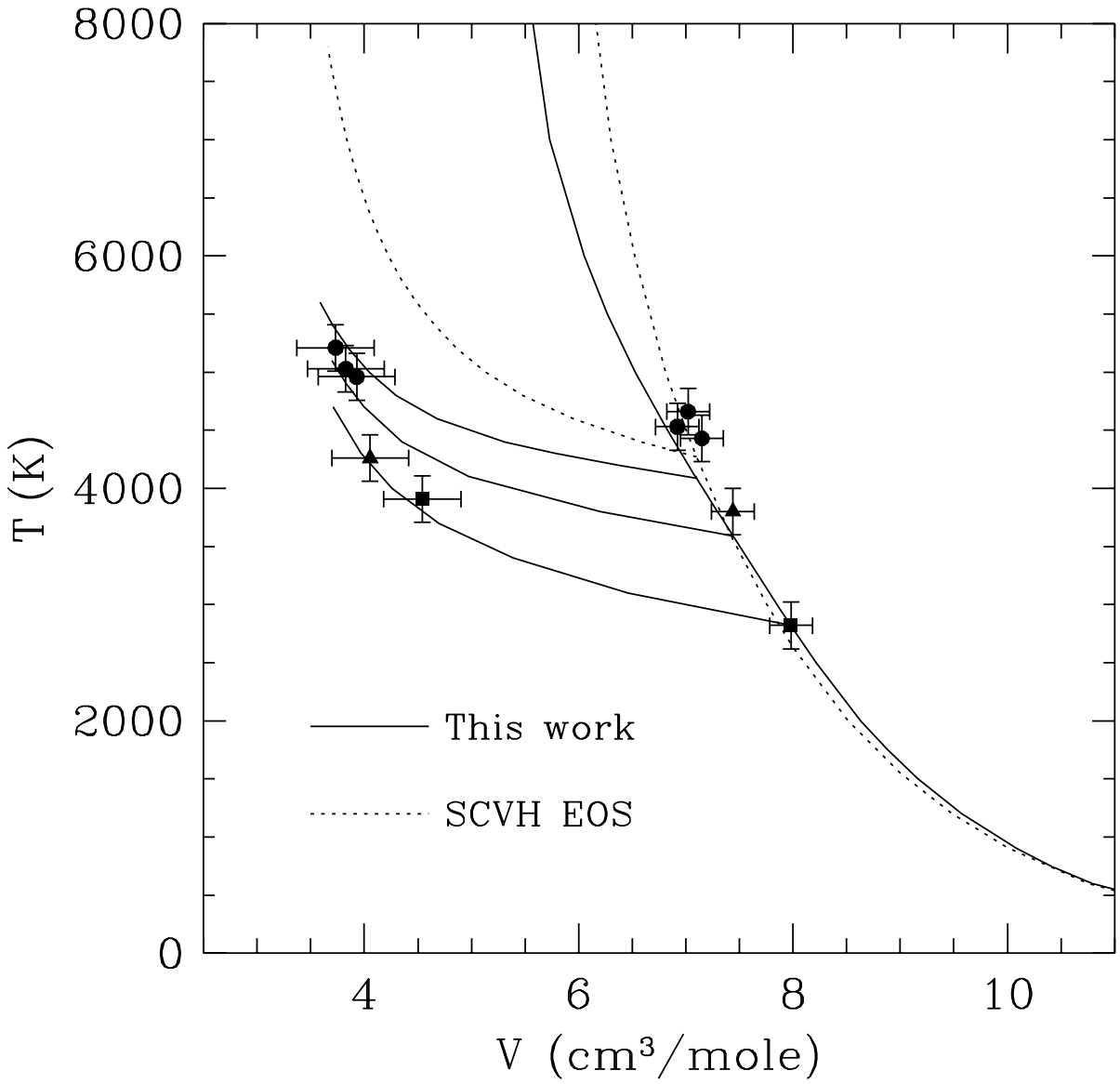
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This work
SCVH EOS